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STATE-RESOLVED REACTION DYNAMICS(U) STANFORD UNIV CA
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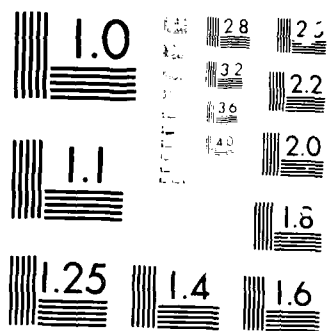
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FINAL REPORT

STATE-RESOLVED REACTION DYNAMICS

F49620-85-C-0021

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During the past three years we have made major progress in three areas: (1) We have studied the simplest of all neutral bimolecular reactions $H + D_2 \rightarrow HD + D$ using one laser to generate fast H atoms in the photolysis of HI in an HI + D_2 mixture and a second laser to detect the HD product in a quantum state specific manner by resonance-enhanced multiphoton ionization of HD via the $E, F \ ^1\Sigma_g^+$ state. (2) We have been able to determine the distribution of impact parameters responsible for the formation of $BaI(v=8)$ product in the beam-gas reaction $Ba + HI$. This required a full rotational analysis of the $BaI \ X^2\Sigma^+$ and $C^2\Pi$ states. (3) We have commenced studies on ion-molecule reactions in which the reagent ion's vibrational and translational energy is controlled and varied in a systematic manner.

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

During the past year we have made major progress in three areas: (1) We have studied the simplest of all neutral bimolecular reactions $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ using one laser to generate fast H atoms in the photolysis of HI in an HI + D_2 mixture and a second laser to detect the HD product in a quantum state specific manner by resonance-enhanced multiphoton ionization of HD via the $\text{E,F } ^1\Sigma_g^+$ state. (2) We have been able to determine the distribution of impact parameters responsible for the formation of $\text{BaI}(v=8)$ product in the beam-gas reaction $\text{Ba} + \text{HI}$. This required a full rotational analysis of the $\text{BaI } X^2\Sigma^+$ and $C^2\Pi$ states. (3) We have commenced studies on ion-molecule reactions in which the reagent ion's vibrational and translational energy is controlled and varied in a systematic manner. It is the last topic that will be described in more length in what follows.

We are investigating the roles played by vibration and rotation in particular reaction systems in an effort to understand the factors that influence the dynamics of ion-molecule reactions. Our approach is to use resonance enhanced multiphoton ionization (REMPI) to produce vibrationally state-selected ion beams. In these studies, ammonia ions are selectively formed with a specific number of vibrational quanta in the ν_2 umbrella bending mode. The effect of vibrational excitation of this mode on the reaction of $\text{NH}_3^+(\bar{X}, v = 0 \text{ to } 9)$ with various neutral reactant partners can be examined over the 1 to 50 eV laboratory energy range in a tandem quadrupole mass spectrometer (Figure 1).

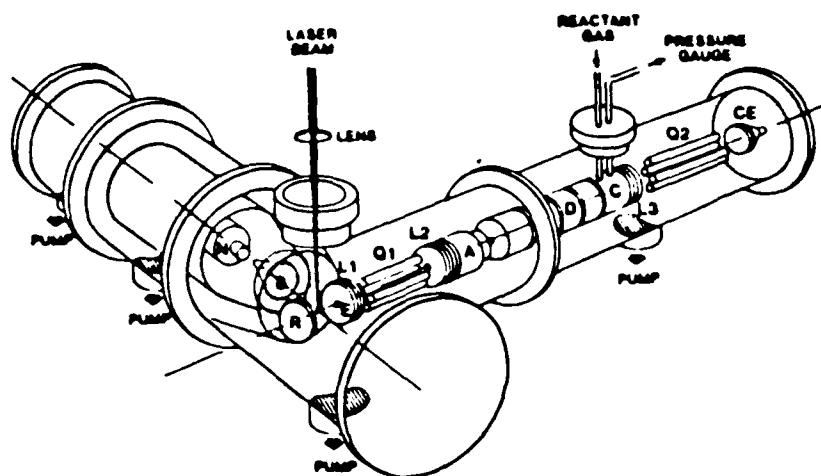


Fig. 1 Schematic diagram of the tandem quadrupole mass spectrometer with laser ionization source.

Two products are observed in the reaction of $\text{NH}_3^+(v)$ with D_2 . Abstraction of a D atom is the dominant reaction channel and vibrational excitation of the ammonia ion is an important contribution to the decomposition of the NH_3D^+ product ion. The NH_2D^+ hydrogen-deuterium exchange product appears as a minor contribution and vibrational excitation does not strongly affect this channel. A simple spectator-stripping model for the deuterium abstraction which includes the NH_3^+ translational and vibrational energy is able to account for the amount of NH_2D^+ formed in the decomposition of the internally excited NH_3D^+ .

The reaction of $\text{ND}_3^+(v)$ with NH_3^+ is more complicated in that there are three independent product channels which individually exhibit very different vibrational behavior. The dominant channel is charge transfer which shows a small vibrational enhancement over the 1 to 12 eV cm kinetic energy range which is consistent with the vibrational overlap and energy mismatch between the ion and neutral states.

The D^+ transfer channel shows a small decrease at low kinetic energies and no effect at higher kinetic energies. The hydrogen abstraction channel shows strong vibrational enhancement above the 3 eV onset (Figure 2). The observation of both the hydrogen abstraction and

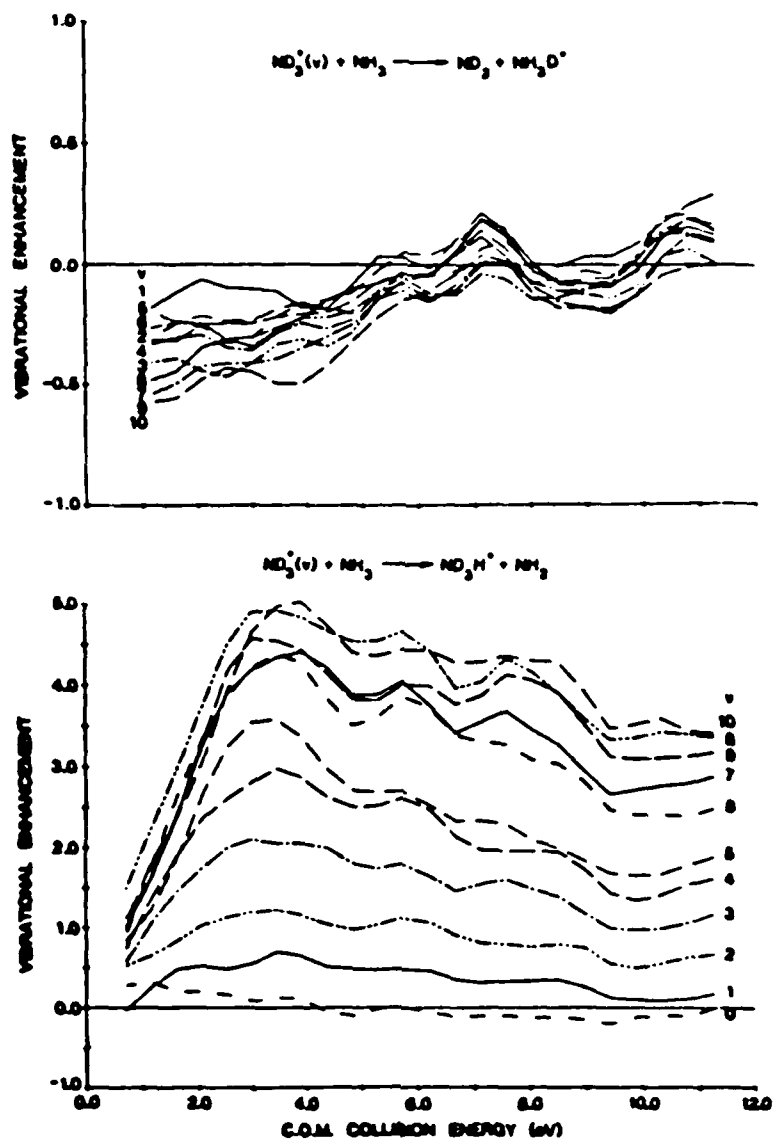
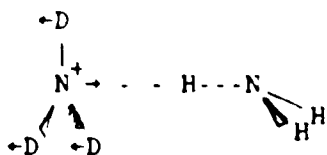
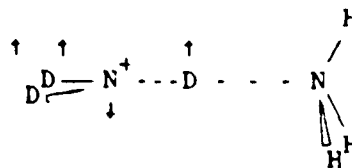


Fig. 2 The effect of vibrational excitation of the ν_2 bending mode on the reaction $ND_3^+(v) + NH_3$. Lower panel: deuteron transfer. Upper panel: hydrogen abstraction.

deuteron transfer channels permits the comparison of the effect of vibration directed along the reaction coordinate (I) to vibration directed perpendicular to the reaction coordinate (II).



I.



II.

The results support the proposition that vibrational excitation of the umbrella bending mode in the hydrogen abstraction channel drives the system more toward the tetrahedral geometry of the product. In addition, studies with $\text{NH}_3^+(\nu) + \text{ND}_3$ indicate that isotopic substitution has a strong effect on the vibrational enhancement in this channel.

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7. "Effect of Internal and Translational Energy on the NH₃⁺(v) + D₂ Ion-Molecule Reaction," by Richard S. Morrison, William E. Conaway, and Richard N. Zare, Chem. Phys. Lett. 113, 433-438 (1985).
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